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Supporting Information

Desolvation and Dehydrogenation of Solvated Magnesium Salts of Dodecahydrododecaborate: Relationship between Structure and Thermal Decomposition

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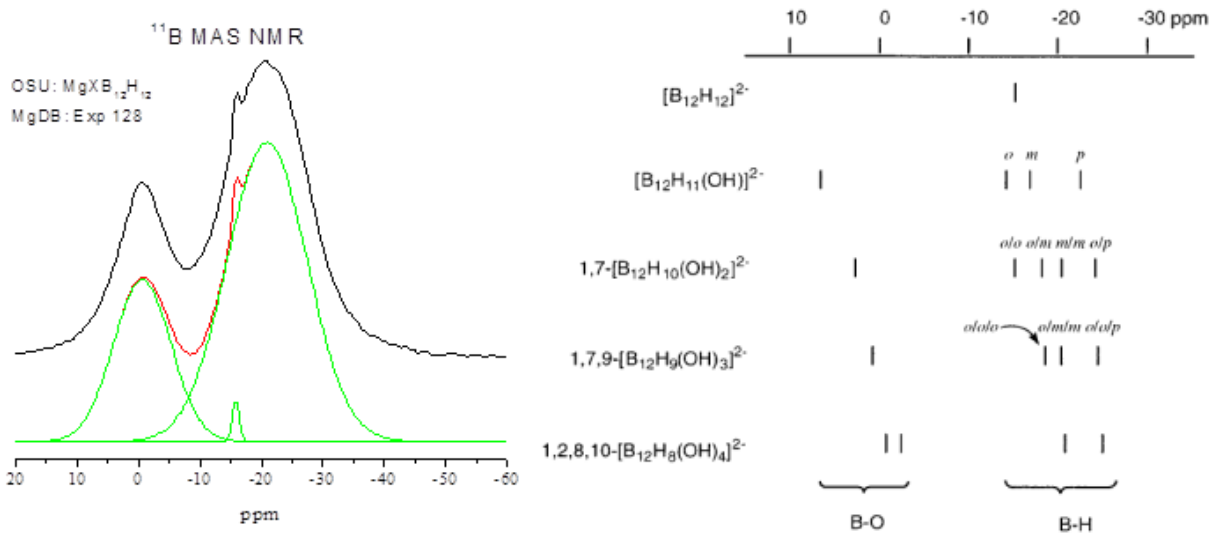

Figure S1. Solid state ^{11}B MAS NMR spectra of dehydrated residual (black) and its decomposition (green) (left); solution ^{11}B NMR spectra of different substitution $B_{12}H_{(12-x)}X_x^{2-}$ (right).[S1]

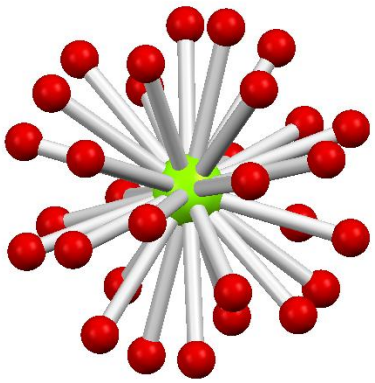

Figure S2. Magnesium coordinated by severely disordered water molecules in $Mg(H_2O)_6B_{12}H_{12}\cdot 6H_2O$.

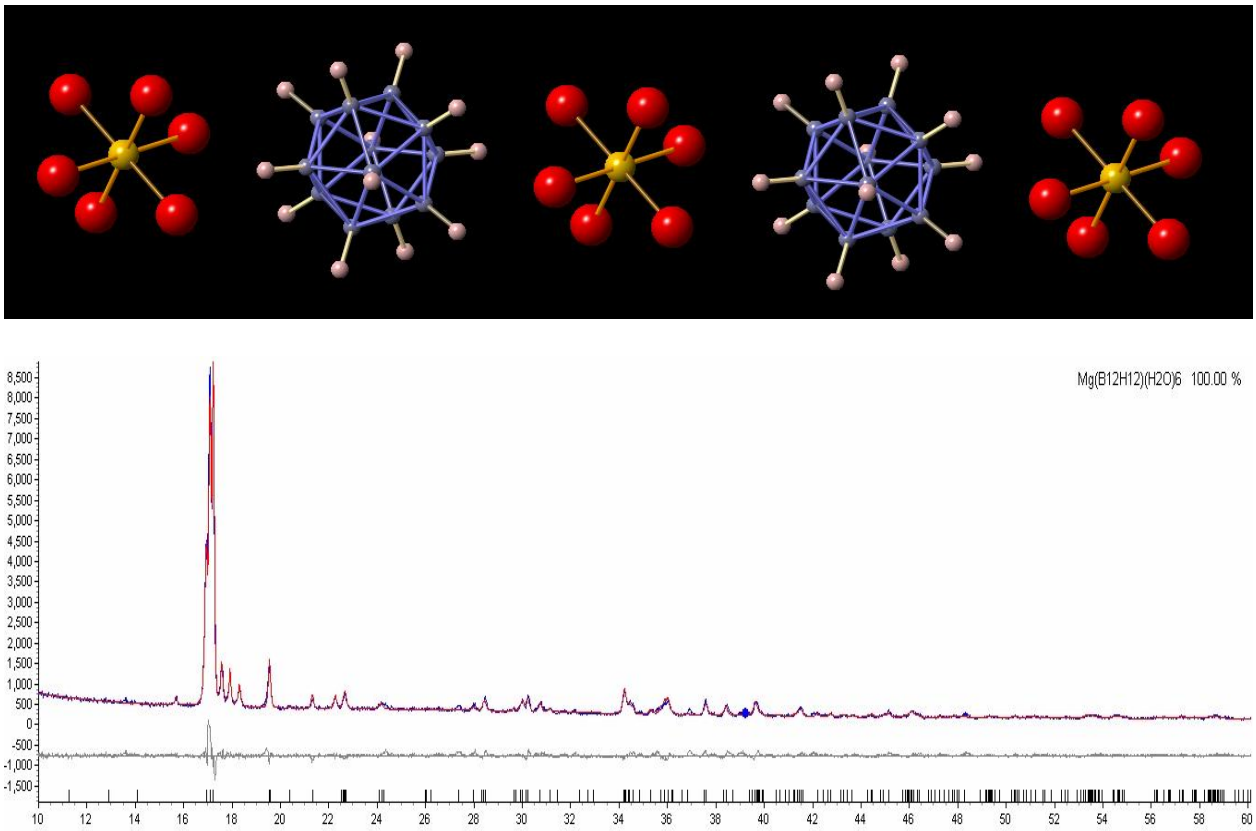

Figure S3. Powder x-ray diffraction pattern Rietveld refinement of $Mg(H_2O)_6(B_{12}H_{12})$ (λ=1.540596Å). Observed data, calculated patterns, and the difference curves are plotted as a blue line, a red line, and a grey line, respectively. The 2-Theta reflections are shown in blue.

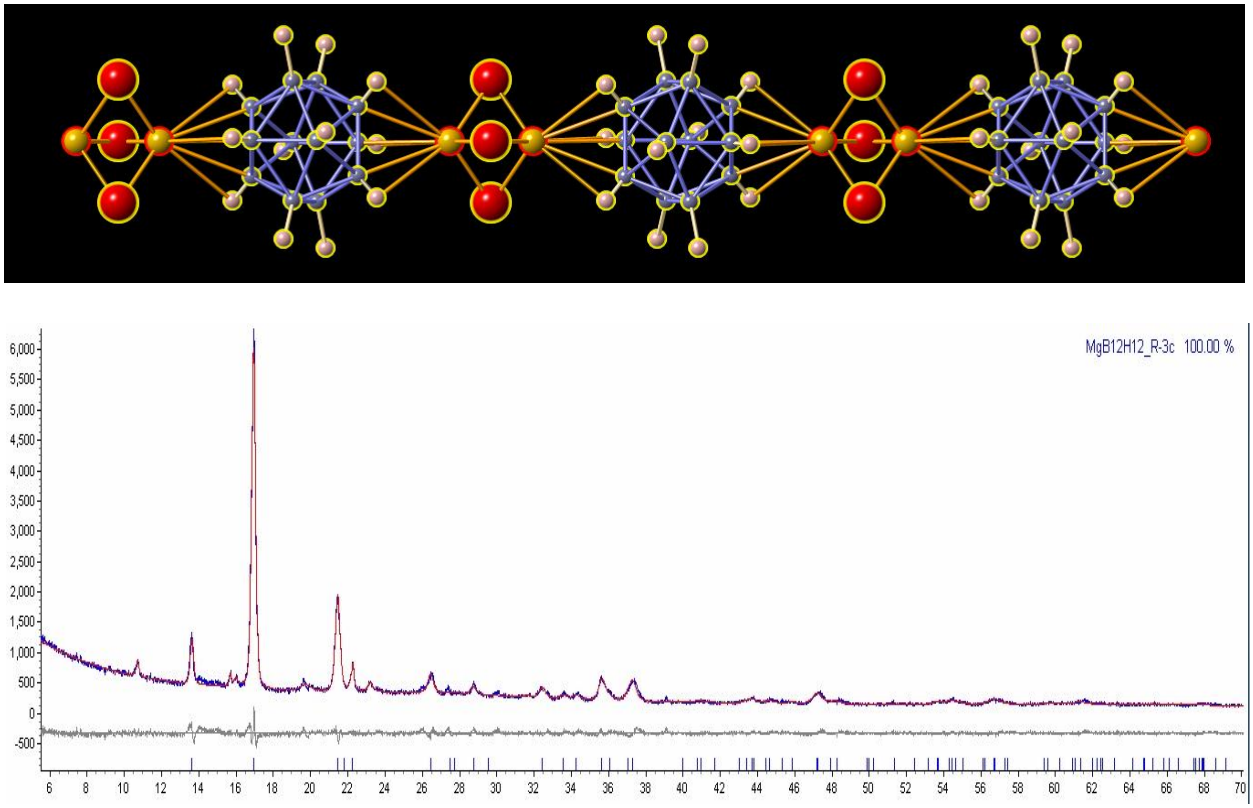

Figure S4. Powder x-ray diffraction pattern Rietveld refinement of $Mg(H_2O)_3(B_{12}H_{12})$ (λ=1.540596Å). Observed data, calculated patterns, and the difference curves are plotted as a blue line, a red line, and a grey line, respectively. The 2-Theta reflections are shown in blue.

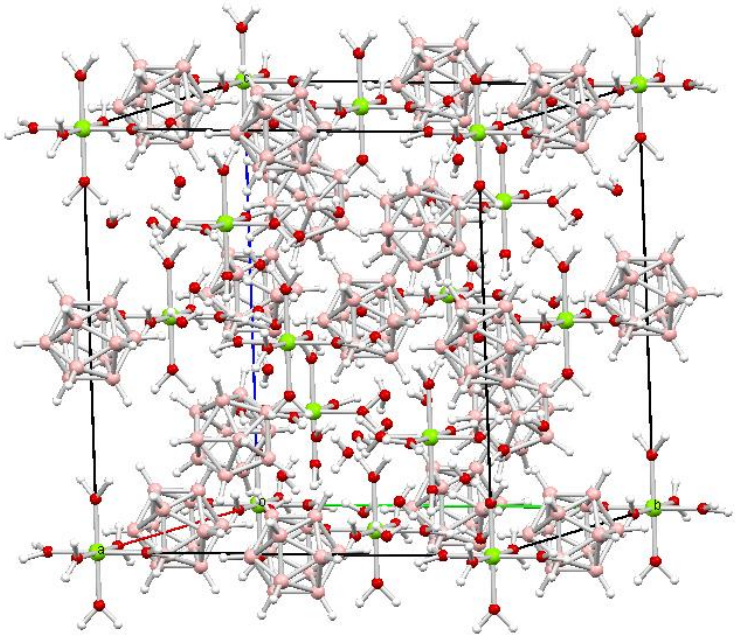

Figure S5. Crystal structure of $Mg(H_2O)_6B_{12}H_{12}\cdot 6H_2O$ previously determined at room temperature.[S2] pink, B; green, Mg; red, O. white, H.

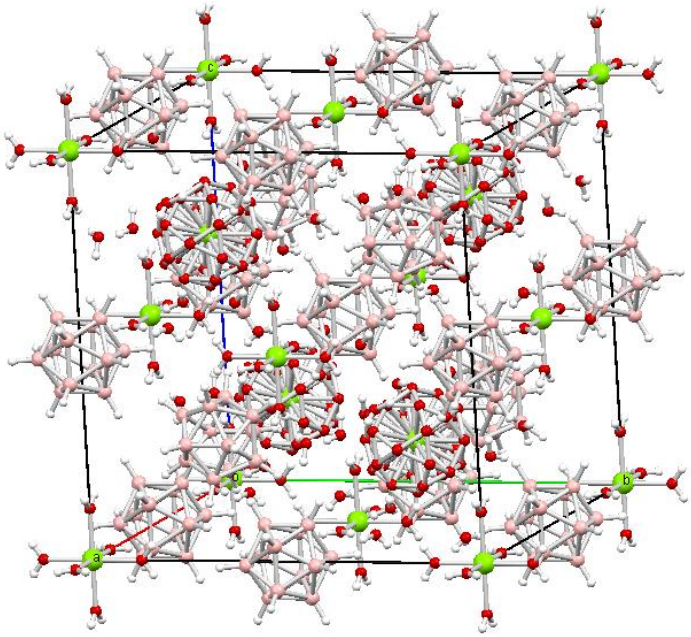

Figure S6. Crystal structure of $Mg(H_2O)_6B_{12}H_{12}\cdot 6H_2O$ re-determined at 150K. pink, B; green, Mg; red, O. white, H.

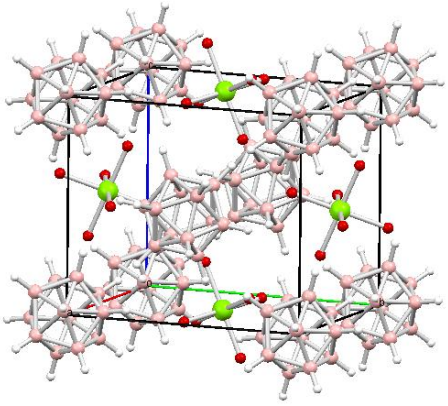

Figure S7. Crystal structure of $Mg(H_2O)_6B_{12}H_{12}$. pink, B; green, Mg; red, O. white, H.

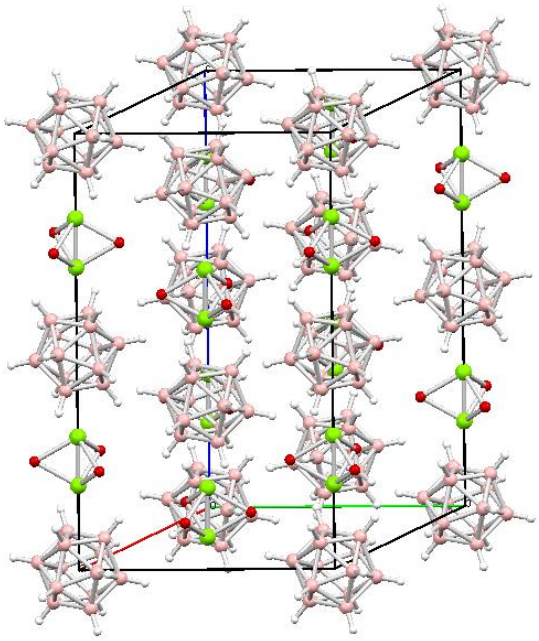

Figure S8. Crystal structure of $Mg(H_2O)_3B_{12}H_{12}$. pink, B; green, Mg; red, O. white, H.

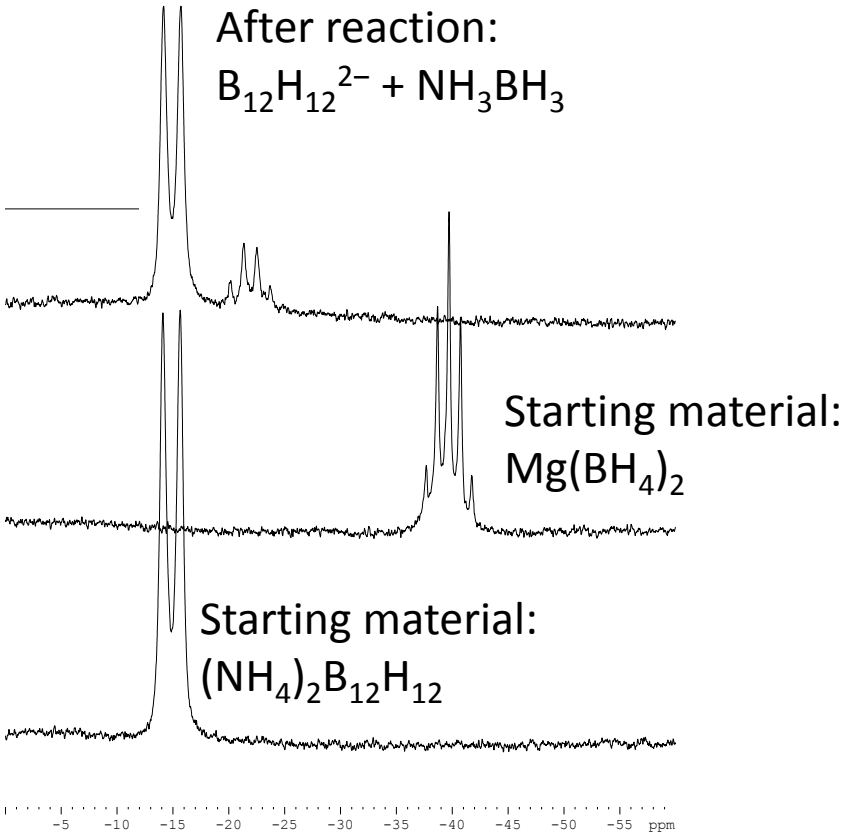

Figure S9. ^{11}B NMR spectra monitoring the reaction of $Mg(BH_4)_2$ + $(NH_4)_2B_{12}H_{12}$ in THF

Table S1. Crystallographic details for $Mg(H_2O)_6B_{12}H_{12}\cdot 6H_2O$ and $Mg(CH_3OH)_6B_{12}H_{12}\cdot 6CH_3OH$

formula	$B_{12}H_{36}MgO_{12}$	$C_{12}H_{60}B_{12}MgO_{12}$
formula weight	382.32	550.63
crystal system	cubic	trigonal
space group	F23	R-3c
Z	8	6
a, Å	16.3149(3)	13.939(2)
c, Å		29.833(6)
T, K	150(2)K	150(2)
V, $Å^3$	4342.63(14)	5019.8(14)
$D_{calc'd}$ ($g\cdot cm^{-3}$)	1.170	1.093
μ (mm^{-1})	0.121	0.097
λ, Å	0.71073	0.71073
no. reflns collected	12944	4824
no. unique reflns	838 (Rint = 0.034)	1289 (Rint = 0.0196)
R1 [I > 2σ (I)][a]	0.0313	0.0383
wR2(all data)[b]	0.0803	0.1200

[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table S2 TOPAS Rietveld Refinement results for $Mg(H_2O)_6B_{12}H_{12}$.

Empirical formula	$B_{12}H_{24}O_6Mg$
Fw	274.22
Space group	$P2_1/c$ (No. 14)
a (Å)	7.855(1)
b (Å)	10.460(1)
c (Å)	9.077 (1)
β (°)	90.62(1)
V (Å^3)	745.75(14)
Z	2
T (K)	295
λ (Å)	1.540596
ρ_{cal} (g cm^{-3})	1.16740(21)
pattern range (2θ, °)	10 to 60
step size (2θ, °)	0.0173
step scan time (s)	0.1
no. of contributing reflns	2899
R_{wp}	0.0853
R_p	0.0637
$R(F^2)$	0.1248

Table S3 TOPAS Rietveld Refinement results for $Mg(H_2O)_3B_{12}H_{12}$.

Empirical formula	$B_{12}H_{18}O_3Mg$
Fw	220.18
Space group	R-3c (No. 167)
a (Å)	10.4597(12)
c (Å)	18.6077(21)
V (Å^3)	1763.1(5)
Z	6
T (K)	295
λ (Å)	1.540596
ρ_{cal} (g cm^{-3})	1.21015(31)
pattern range (2θ, °)	5 to 70
step size (2θ, °)	0.0173
step scan time (s)	0.1
no. of contributing reflns	3757
R_{wp}	0.0709
R_p	0.0531
$R(F^2)$	0.1493

Table S4 Atomic coordinates for $Mg(H_2O)_6B_{12}H_{12}$.

Atoms	*x*	*y*	*z*	*occ*	*Beg*
$B_{12}H_{24}O_6Mg$					
Mg	0.5	0	0.5	1	3.8223
O(1)	0.5060(23)	0.9207(18)	0.2883(17)	1	2.6808
O(2)	0.7210(28)	0.1069(19)	0.4600(21)	1	6.3083
O(3)	0.3630(24)	0.1619(17)	0.4150(19)	1	6.6768
B(1)	0.0245(57)	0.0490(28)	0.1798(34)	1	-1.0378
B(2)	0.9834(63)	0.8382(45)	0.9709(43)	1	6.0366
B(3)	0.8922(48)	0.9141(36)	0.1308(40)	1	-0.7805
B(4)	0.8792(53)	0.0965(35)	0.8867(41)	1	1.0650
B(5)	0.8277(52)	0.0737(43)	0.0786(44)	1	2.6761
B(6)	0.8024(62)	0.9434(49)	0.9496(55)	1	4.9832
H(1)	0.04015	0.08031	0.294513	1	3.1214
H(2)	0.9728566	0.7350124	0.9524568	1	3.1214
H(3)	0.8233039	0.8592372	0.2141141	1	3.1214
H(4)	0.8022605	0.1580515	0.8145162	1	3.1214
H(5)	0.7178697	0.1206897	0.1288621	1	3.1214
H(6)	0.6762807	0.907284	0.9174626	1	3.1214

Table S5 Atomic coordinates for $Mg(H_2O)_3B_{12}H_{12}$.

Atoms	*x*	*y*	*z*	*occ*	*Beg*
$B_{12}H_{18}O_3Mg$					
Mg	0	0	0.1940(1)	0.5	4.407
O	0	0.1688(14)	0.75	1	4.515
B(1)	0.1649(22)	0.1617(15)	0.016(1)	1	2.143
B(2)	0.9033(14)	0.9067(18)	0.071(1)	1	2.143
H(1)	0.291(13)	0.266 (11)	0.0277 (44)	1	2.143
H(2)	0.837(13)	0.846(11)	0.0966(52)	1	2.143

References:

S1. T. Peymann, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem*., 2000, **39**, 1163-1170.

S2. I. Tiritiris and T. Schleid, *Z. Anorg. Allg. Chem*., 2004, **630**, 541-546.